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(54) Title: SELF–WARMING HAIR CONDITIONING COMPOSITIONS

(57) Abstract

An essentially anhydrous hair conditioning composition comprising: (a) one or more microporous materials each of which has an average pore size larger than the critical diameter of a water molecule; (b) carrier molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials; and (c) conditioner molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials. The invention also relates to a method for conditioning hair with warming which comprises administering to the hair, with water, the hair conditioner compositions of the invention.

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# SELF-WARMING HAIR CONDITIONING COMPOSITIONS

## FIELD OF THE INVENTION

This invention concerns processes and compositions for the treatment of human hair. More particularly the invention concerns a hair conditioner composition and a conditioning shampoo composition that provide a noticeable increase in temperature during use and that provide good conditioning properties to the hair.

## BACKGROUND OF THE INVENTION AND PRIOR ART

When treating hair with conditioner, it would be desirable for the conditioner being used to increase in temperature during actual use. More specifically it would be desirable for the conditioner to increase in temperature after being added to hair that is already wet (for example, after shampooing). Alternatively such a conditioner could be added to dry hair and then after water is added, there would be an increase in temperature in said conditioner. Finally, such a conditioner could be put on hair simultaneously with water and the conditioner would increase in temperature. Such increases in temperature are referred in this specification as self-warming. Such self-warming would provide the consumer with a feeling of comfort and relaxation, as well as supplying the consumer with a "signal" that the conditioner composition is working.

A self-warming composition which is presently on the market is Lux Super Rich Self Warming Conditioner. It is an anhydrous glycol containing composition which generates heat through the dissolution of the glycol in water. By contrast the compositions of the present invention generate heat when water adsorbs into the pores of the microporous materials. Anhydrous glycol containing products increase in temperature on application of water, 7 to 8 degrees C under normal conditions of use on the hair. The compositions of the present invention will often increase in temperature significantly more upon application of water during use in the hair.

It is an object of the present invention to provide an improved hair conditioner which provides increased self-warming hair conditioner composition during use (i.e., when applied to hair with water) while not decreasing the conditioning provided, and in some cases increasing the conditioning that is provided.

## BRIEF SUMMARY OF THE INVENTION

The invention relates to hair conditioner compositions which are essentially anhydrous that comprise:

(a) one or more microporous materials each of which has an average pore size larger than the critical diameter of a water molecule;

(b) carrier molecules or molecular aggregates that have critical diameters larger than the largest

average pore size of the microporous materials; and

(c) conditioner molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials.

The invention also relates to a process for treating hair which comprises administering to said hair, the hair conditioner composition described above.

The invention also relates to a conditioning shampoo composition that provides a noticeable increase in temperature during use.

The invention also relates to a process for treating hair which comprises administering to said hair, the conditioning shampoo composition described above.

The hair conditioner compositions of the invention and the conditioning shampoo compositions provide increased self-warming during use (i.e., when applied to hair with water) while not decreasing the hair conditioning provided and in some cases increasing the hair conditioning provided. This is an unexpected result, since the hair conditioner compositions of the invention comprise microporous materials such as molecular sieves which are a solid particulate material which would be expected to decrease the conditioning properties of the compositions of the invention as compared to compositions without microporous materials or molecular sieves. In fact the compositions of the invention

have the same or increased conditioning properties as noted above.

## DETAILED DESCRIPTION OF THE INVENTION

Hair conditioner compositions of the invention include rinse-off and leave-in conditioners.

As used herein "essentially anhydrous" means less than about 2 weight % preferably less than about 1 weight % of water.

Unless other indicated, as used herein % means weight %. All of the starting materials described herein are either known or can be prepared according to known methods. The essentially anhydrous hair conditioner compositions of the invention comprise:

(a) one or more microporous materials each of which has an average pore size larger than the critical diameter of a water molecule;

(b) carrier molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials; and;

(c) conditioner molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials.

It is noted that each of the one or more microporous materials referred to above has an average pore size larger

than the critical diameter of a water molecule. The size of a water molecule is about 3.2 Angstroms. It is also noted that microporous materials with an average pore size of 3 Angstrom are used in compositions described below. Even though some of such microporous materials have too small a pore size to adsorb water, enough of such microporous materials have a large enough pore size to be useful in the compositions of the invention.

The microporous materials may be selected from the group consisting of inorganic salts such as crystalline metal silicates such as sodium potassium aluminum silicate, aluminum silicate, calcium aluminum silicate, activated alumina (aluminum oxide), clays which are silicates, known as diatomaceous silicas, bentonites and clays these are aluminum oxides and silicon oxides, and crystalline metal aluminosilicates. Among the crystalline metal aluminosilicates which may be employed are aluminosilicates which range in average pore size from about 3 Angstroms to about 10 Angstroms.

In general, the average pore size for the sieves that are used in the compositions of the invention can range from about 3 Angstroms to about 13 Angstroms or larger. more preferably, the average pore size of the sieves can range from about 3 Angstroms to about 1 0 Angstroms.

The tradenames of these aluminum silicates include Aldrich 3A Sieves, Aldrich 1 OX Sieves, and Sylosiv A3 Sieves, and Sylosiv A4 Sieves.

PQ Corporation is another molecular sieve supplier and the material that they supply, is an aluminosilicate is called Advera 401 N.

Organic resins such as activated charcoal may also be employed where the average pore size of the organic resins meets the parameters described above.

The microporous materials are normally present in a concentration of from 5% to 60%, preferably from 1 0 to 40% by weight based on the total weight of the hair treatment composition, or more preferably 15 to 30% by weight based on the total weight of the hair treatment composition.

Carrier materials must have a critical diameter larger than the largest average pore size of the microporous materials selected. With respect to the resulting anhydrous hair care composition, as long as most of the pores in the microporous material are unoccupied there will be a heating effect on the addition of water.

The selected carrier materials have to be water soluble or water dispersible otherwise they could not be used on hair in combination with water.

Suitable carrier materials include hydrophilic glycols, polyethylene glycols, and polar solvents like alcohols. Any carrier used must either be water soluble or water dispersible.

The following list of hydrophilic glycols or polyhydric alcohols which may be used in compositions of the invention is meant to be illustrative and not limiting. These hydrophilic glycols are as follows: propylene glycol, ethylene glycol, glycerin, sorbitol, butanediol, butylene glycol, and mixtures thereof.

The following list of polyethylene glycols which may be used in compositions of the invention is meant to be illustrative and not limiting. These polyethylene glycols are as follows: PEGs -4, -6, -8, -9, -10, -12, -14, -16, -18, -20, -200, -400 and -600. Also included are beheneth -5 and -10, peg-7 betanaphthol and PEG-15 butanediol. Also included are buteth-3 carboxylic acid, butoxynol-5 and -19, PEG-8 C12-18 ester, C12 13 pareth-7 carboxylic acid, Cl 1 -1 5 pareth-7 carboxylic acid, Cl 2 -15 pareth-7 carboxylic acid, C14 -15 pareth-8 carboxylic acid, PEG-8 caprate, PEG-8 caprylate, PEG-8 caprate/caprylate, PEG -6, and -8 caprylic/capric glycerides, capryleth -6 and -9 carboxylic acids, ate, PEG-8 caprylate. Also included are ceteareth -2, -3, -4, -5, -5, -6, -7, -8, -10, , -11, -12, -13, -15, -6, -17, -18, and -20; choleth -1 0 and -20; PEG-3 cocamide, PEG-5 cocamide, PEG-6 cocamide, PEG-7 cocamide, PEG-1 1 cocamide, PEG-20 cocamide; PEG-2 cocamine, PEG-3 cocamine, PEG-5 cocamine, PEG-10 cocamine, PEG-15 cocamine, and PEG-20 cocamine; PEG-5 cocoate, PEG-8 cocoate, PEG-1 5 cocoate; coceth-3, 5, and -8; PEG-2 dilaurate, PEG-4 dilaurate, PEG-6 dilaurate, PEG-8 dilaurate, PEG-12 dilaurate, PEG-20 dilaurate, PEG-4 dioleate, PEG6 dioleate, PEG-8 dioleate, PEG-1 0 dioleate, PEG-1 2 dioleate, and isosteareth-2, isosteareth-3, isosteareth-10, isosteareth-12, and isosteareth-20;

isoceteth-10, and -20; isodeceth -4, -5, and -6; isostereath -2, -3, 10, -12, and -20; PEG-3 lauramine oxide; PEG-2 laurate, PEG-4 laurate, PEG-6 laurate, PEG-8 laurate, PEG-9 laurate, PEG-10 laurate, PEG-12 laurate, PEG-14 laurate, and PEG-20 laurate; laureth -1, -2, -3, -4, -5, -6, -7, -8, -9, -10, -11, -12, -13, -14, -15, -16,and -20; oleth 2, -3, -4, -5, -6, -7, -8, -9, -10, 12, -15, -16, and -20; stereath -2, -3, -4, -5, -6, -7, -10, -11, -13, -1 4, -15, -16, and -20; and trideceth -3, -5, -6, -9, -10, -11, -12, and -15.

The following list of polar solvents like alcohols which may be used in compositions of the invention is meant to be illustrative and not limiting. These polar solvents like alcohols are as follows: methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol and isopropanol and mixtures thereof.

Carrier materials may be included in compositions of the invention in a weight % range of about 40% to about 90%, more preferably about 60 to about 80%.

Conditioner materials are selected from the group consisting of quaternary ammonium compounds, amidoamines, silicones, cationic polymers, hydrocarbons, fatty alcohols, either alone or in combination. Any conditioner material which is used in a composition of the invention must have a critical diameter that is larger than the largest pore average size of the microporous materials.

The following list of silicones which may be used in compositions of the invention is meant to be illustrative

and not limiting. These silicones are as follows: a polyalkyl siloxane, a polyaryl siloxane or a polyalkylaryl siloxane.

Mixtures of volatile silicones as cyclotetrasiloxane, cyclopentasiloxane, or cyclohexasiloxane are useful. Mixtures of the nonvolatile silicone compounds are also useful. The so-called "rigid silicones", as described in U.S. Patent 4,902,499, herein incorporated by reference, having a viscosity above 600,000 cs at 20C and a weight average molecular weight of at least about 500,000, also are useful in compositions of the present invention. A phenyltrimethicone also is useful as a nonvolatile silicone compound. Also useful is a mixture of a low molecular weight silicone fluid and a higher molecular weight silicone gum. Silicones which are useful in compositions of the invention are described in US patent 5,656,280 which is hereby incorporated by reference.

Non-volatile silicones include siloxane or siloxane mixtures having a viscosity of greater than 1 0 centistokes. Nonlimiting examples include dimethicone, dimethiconol, amodimethicones, phenyl trimethicone and silicone copolyols.

The following list of cationic polymers which may be used in compositions of the invention is meant to be illustrative and not limiting. These cationic polymers are as follows: Guar hydroxypropyltrimonium chloride, poly(dimethyidiallylammonium chloride), poly(dimethyl butenyl ammonium chloride)- bis (triethanolammonium chloride), Poly (dipropyldiallylammonium chloride), Poly

(methyl-beta propaniodiallylammonium chloride), Poly (diallylpiperidinium chloride), Poly (vinylpyridinium chloride), quaternised poly (vinyl alcohol), quaternised poly (dimethylaminoethylmethacrylate) and mixtures thereof. These cationic polymers are described in U.S. Patent 5,580,550 which is hereby incorporated by reference.

The following list of hydrocarbons which may be used in compositions of the invention is meant to be illustrative and not limiting. These hydrocarbons are as follows: nonane, octane, heptane, tert-pentane, dodecane, decahexane, decane, heptadecane, trimethylheptane, trimethylhexane, 4-methylheptane, 4-methyldecane, isobutane, isopentane, isooctane, hexane, isododecane, polydecene, mineral oil, paraffin wax and isohexadecane. Other exemplary volatile hydrocarbons are depicted in the general structural formula I wherein n ranges from 2 to 5.

$$H_3C(C(CH_3)_2\text{-}CH_2)_n\text{-}CH(CH_3)_2.$$

Another exemplary hydrocarbon is ISO-PAR M (a Cl 3-Cl 4 isoparaffin available from Exxon Chemical Co. Baytown Texas). These compounds are described in U.S. Patent 5,656,280 which is hereby incorporated by reference. Also included among volatile hydrocarbons which can be used in compositions of the invention are mineral oil, paraffins, fatty acids, caprylic/capric triglyceride, caprylic/capric diglyceryl succinate, propylene glycol dicaprylate/dicaprate, mineral jelly, acetylated lanolin, M-quat 40, oil soluble lipo-protein, collagen/lanolin oil blend, mineral oil and lanolin alcohol, cetyl acetate,

lanolin oil, isopropyl palmitate and lanolin oil, silk powder, decyl neopentanate, jojoba oil, and propoxylated polyol.

The following list of quaternary ammonium compounds which may be used in compositions of the invention is meant to be illustrative and not limiting. These compounds have the general structural formula: N[R 1 R2R3R4]+ X-where R, is an alkyl group including from about 8 to about 18 carbon atoms, R2 is selected from the group consisting of an alkyl group including from about 8 to about 18 carbon atoms, a hydrogen atom, a methyl group, an ethyl group, a hydroxymethyl group and a hydroxyethyl group, R4 is selected from the group consisting of a hydrogen atom, a methyl group, an ethyl group, a hydroxymethyl group, and a hydroxyethyl group; and X is an anion. The quaternary nitrogen of the quaternary ammonium compound can also be a component of a heterocyclic moiety such as morpholine or pyridine. The anion can be an anion such as chloride, methosulfate, ethosulfate. nitrate, bromide. tosylate. acetate or phosphate.

The quaternary ammonium compounds have one or two long chain alkyl groups having from about 8 to about 18 carbon atoms. the long chain alkyl groups can also include in addition to, or in replacement of carbon and hydrogen atoms, ether linkages or similar water solubilizing linkages the remaining two or three substituents of the quaternary nitrogen can be hydrogen or benzyl; or short chain alkyl or hydoxyalkyl groups such as methyl ethylhydroxymethyl or hydroxyethyl groups, or combinations thereof either diether of the same or different identity.

Exemplary quaternary ammonium compounds include but are not limited to lauratrimonium chloride, quaternium -16, lauralkonium chloride, dicetyldimonium chloride, cetylpyridinium chloride, soyatrimonium chloride, mytrimonium chloride, cetrimonium chloride, PEG-2 cocomonium chloride, PEG 2 cocoyl quaternium -4, PEG 2 oleyl quarenium 4 polyquaternium -6,-7, -11, -5, -24, and mixtures thereof. these quaternary ammonium compounds are described in U.S Patent 5,656,280 which is hereby incorporated by reference. Other water-soluble ammonium compounds include distearyl dimonium chloride, and behenyl trimmonium chloride.

The following list of amidoamines which may be used in compositions of the invention is meant to be illustrative and not limiting. These amidoamines Include those described in U.S. Patent 5,328,685 which is hereby incorporated by reference.

Amidoamines include but are not limited to diethylaminoethylstearamine, isosteamidopropyldimethylamine, cocamidopropyldimethylamine, ricinoleamido propyldimethylamine, oleamidopropyldimethylamine, behenamidopropyldimethylamine, palmitamidopropyldimethylamine, stearamidoethyldiethylamine, stearamidylpropyldiethylamine, stearamidopropyldimethylamine soyamido propyldimethylamine and dimethylaminopropyl myristamide.

The following list of fatty alcohols which may be used in compositions of the invention is meant to be illustrative and not limiting. These fatty alcohols include a fatty

alcohol or fatty acid, or derivative thereof, or a mixture of any of these having a chain length of from about 8 to about 36 carbon atoms. More preferably from about 12 to about 22 carbon atoms. These materials may be predominantly linear or may be branched. Preferred are stearyl alcohol, cetyl alcohol, behenyl alcohol, lauryl alcohol, myristyl alcohol, and coco alcohol.

Conditioner materials may be included in compositions of the invention in a weight per cent range of about 2% to about 45 %, more preferably about 10 to about 30%.

Optional ingredients which can be used in compositions of the invention are now described.

Nonionic surfactants suitable for use in compositions of the invention include condensation products of aliphatic C8-C18 primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide, and generally having from 6 to 30 ethylene oxide groups.

Other suitable nonionics include mono- or di-alkyl alkanolamides. Examples include coco mono- or diethanolamide and coco mono-isopropanolamide. Further suitable nonionic surfactants are the alkylpolyglycosides (APG's). Typically, the APG is one which comprises an alkyl group connected (optionally via a bridging group) to a block of one or more glycosyl groups.

Amphoteric and zwitterionic surfactants suitable for use in compositions of the invention may include alkyl amine

oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycinates, alkyl carboxyglycinates, alkyl amphopropionates, alkylamphoglycinates alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms.

Examples include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl betaine and sodium cocamphopropionate.

Further surfactants which may be suitable for use in conditioning shampoos in accordance with the invention include one or more anionic surfactants instead of or in addition to any of those surfactants mentioned above. Those surfactants must be dispersed or mixed in glycols, PEGS, etc.

Suitable anionic surfactants are the alkyl sulphates, alkyl either sulphates, alkaryl sulphonates, alkaroyl isethionates, alkyl succinate, alkyl sulphosuccinates, N-alkoyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpho-olefin sulphonates, especially their sodium, magnesium, ammonium and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl ether phosphates and alkyl ether carboxylates may contain from one to 1 0 ethylene oxide or propylene oxide units per molecule, and preferably contain 2 to 3 ethylene oxide units per molecule.

Examples of suitable anionic surfactants include sodium oleyl succinate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, sodium dodecylbenzene sulphonate, triethanolamine dodecylbenzene sulphonate, sodium cocoyl isethionate, sodium lauroyl isethionate and sodium N-lauryl sarcosinate. The most preferred anionic surfactants are sodium lauryl sulphate, triethanolamine lauryl sulphate, triethanolamine monolauryl phosphate, sodium lauryl ether sulphate 1 EO, 2EO and 3EO, ammonium lauryl sulphate and ammonium lauryl ether sulphate 1 EO, 2EO and 3EO.

As further optional components for inclusion in the compositions of the invention, the following may be mentioned: pH adjusting agents, viscosity modifiers, cosmetic fillers such as talc, kaolin; pearlescers, opacifiers, suspending agents, preservatives, coloring agents, dyes, proteins, herb and plant extracts, polyols and other moisturising.

Compositions of the invention can be made by using processes which are known in the art or by using processes which are analogous to those known in the art. Compositions of the invention can be made by using starting materials which are known in the art or by using starting materials which are obtainable from materials that are known in the art.

Compositions of the invention are used in a manner known for leave-in and wash-out conditioners. Namely, the hair is wet and then conditioner or conditioning shampoo is applied to the hair.

If the conditioner is a leave-in conditioner, it can be applied to wet or dry hair. If applied to dry hair, then water is added after such application. If the conditioner is a wash-out conditioner, the hair is the rinsed after application.

The self-warming that occurs with the use of the hair conditioner compositions arises when water molecules adsorb into the pores of the microporous materials. This step releases heat which is felt as self-warming. Up to a 170C increase or more, typically increases of 150C or more are achieved with compositions of the invention. 120C increase or more, or increases of 100C or more can also be achieved with compositions of the invention. The temperature increase, being referred to above, which is caused by compositions of the invention is the change which occurs in degrees C when 70 parts of composition is mixed with 30 parts water at room temperature.

Compositions of the invention are made by processes known in the art, or analogous to those known in the art using starting materials which are known in the art.

Ingredients which are used in compositions of the invention may fall within the following ranges of weight ratios:

| INGREDIENT | WEIGHT % |
|---|---|
| | |
| Microporous materials | 5-60 |
| | |
| Carrier ingredients | 20-80 |
| | |
| Conditioner ingredients | 1-30 |

Examples of the invention shown below are made by processes known in the art, or analogous to those known in the art.

Examples of the invention are as follows:

**EXAMPLE 1 -- COMPARATIVE EXAMPLE**

**or other** microporous materials

Conditioner -- without molecular sieves

| INGREDIENT | WEIGHT % |
|---|---|
| | |
| PEG 200 | 71.15 |
| CETEARYL ALCOHOL | 2.5 |
| BEHENTRIMONIUM CHLORIDE | 2.0 |
| STEARETH-2 | 1.0 |
| STEARETH-21 | 1.0 |
| GLYCERIN | 18.6 |
| PANTHENOL | 0.1 |
| DIMETHICONE | 3.0 |
| FRAGRANCE | 0.65 |

**Example** 2-- Conditioner with molecular sieves or microporous material

| INGREDIENT | WEIGHT % |
|---|---|
| PEG 200 | 50.45 |
| CETEARYL ALCOHOL | 2.5 |
| BEHENTRIMONIUM CHLORIDE | 2.0 |
| STEARETH-2 | 1.0 |
| STEARETH-21 | 1.0 |
| PANTHENOL | 0.1 |
| GLYCERIN | 18.6 |
| CITRIC ACID | 0.7 |
| DIMETHICONE | 3.0 |
| SODIUM POTASSIUM ALUMINO-SILCATE 3 Angstroms | 20.0 |
| FRAGRANCE | 0.65 |

**Example 3- conditioner with molecular sieves or microporous materials**

| INGREDIENT | WEIGHT % |
|---|---|
| PEG 200 | 55.45 |
| CETEARYL ALCOHOL | 2.5 |
| BEHENTRIMONIUM CHLORIDE | 2.0 |
| STEARETH-2 | 1.0 |
| STEARETH-21 | 1.0 |
| GLYCERIN 99.7% | 18.6 |
| PANTHENOL | 0.1 |
| CITRIC ACID | 0.7 |
| DIMETHICONE | 3.0 |
| SODIUM POTASSIUM ALUMINO SILICATE 3 Angstroms | 15.0 |
| FRAGRANCE | 0.65 |

Example 4--conditioner with microporous materials or sieves

| INGREDIENT | WEIGHT % |
|---|---|
| PEG 200 | 51.15 |
| CETEARYL ALCOHOL | 2.5 |
| BEHENTRIMONIUM CHLORIDE | 2.0 |
| STEARETH-2 | 1.0 |
| STEARETH-21 | 1.0 |
| GLYCERIN 99.7% | 18.6 |
| PANTHENOL | 0.1 |
| DIMETHICONE | 3.0 |
| SODIUM POTASSIUM ALUMINO SILCATE 3 Angstroms | 20.0 |
| FRAGRANCE | 0.65 |

**Example 5**

**Self-warming Shampoo can be prepared with ingredients in the following ranges:**

| INGREDIENT | WEIGHT % |
|---|---|
| PEG -200 | Qs to 1 00 |
| DIMETHICONE | .5 TO 1 |
| SILICA | .1 to 5 |
| GUAR HYDROXYPROPYLTRIMONIUM CHLORIDE | .05 to 1 |
| LAURYL HYDROXYETHYL IMIDAZOLINE 100% | 5 to 50 |
| SODIUM POTASSIUM ALUMINOSILICATE A3 | 20 |
| ADDITIVES | .01 to 5 |

**TABLE I**

| COMPOSITION | WET COMBING TOTAL ENERGY mi | WET COMBING MAX LOAD G FORCE |
|---|---|---|
| | | |
| EXAMPLE1 | 12.97 | 14.48 |
| EXAMPLE 2 | 11.93 | 12.97 |

The above table I demonstrates that compositions of the invention which comprise molecular sieves (example 2) have the same or even better wet combing properties than compositions without sieves (example 1) and that therefore, the compositions of the invention have the same or even better conditioning properties than compositions without molecular sieves.

**Table II**

Summary of Self Warming Compositions-Effect of Molecular Sieve Addition

| COMPOSITION | WATER DILUTION TEMP. IN DEGREES C[1] | PORE SIZE IN ANG. STROMS | WT. % MOL. SIEVES |
|---|---|---|---|
| 100% PEG 200 | +8 | NA[2] | 0% |
| 100% GLYCERIN | 0 | NA | 0% |
| 90% PEG 200 +10%ALDRICH 3A | +11 | 3 | 10% |
| 90% GLYCERIN +10% ALDRICH 3A | +6 | 3 | 10% |
| 90% PEG 200 9+10% ALDRICH 13X[4] | +10 | 9-10 | 10% |
| 90% GLYCERIN +10% ALDRICH 13X | +9 | 9-10 | 10% |
| 90% PEG 200 +10% ZEOLEX 35-P[5] | +10 | NA | 10% |
| 90% GLYCERIN +10% ZEOLEX 35-P | 0 | NA | 10% |
| 90% PEG 200 +10% SYLOSIV 3A[3] | +19 | 3 | 10% |
| 90% GLYCERIN +10%SYLOSIV 3A | +11 | 3 | 10% |
| CONDITIONER EXAMPLE 1 (Comparative example without molecular sieves) | +7 | Na | 0% |
| CONDITIONER EXAMPLE 2 | +18 | 3 | 20% |
| CONDITIONER EXAMPLE 3 | +11 | 3 | 15% |
| CONDITIONER EXAMPLE 4 | +18 | 3 | 20% |

**TABLE NOTES**

1) Water dilution temp increase is the change in temperature in degrees C when 70 parts of composition is mixed with 30 parts of water.
2) NA is not applicable.
3) Sylosiv 3A is a tradename of the molecular sieves supplied by WR Grace.
4) Aldrich 13X and Aldrich 3A are tradenames of molecular sieves supplied by Aldrich Chemical.
5) ZEOLEX 35-P is a tradename of amorphous sodium aluminosilicate supplied by JM Huber.

The above table 11 demonstrates that compositions of the invention (examples 2,3,4) raise temperature on mixing with water significantly more degrees C than compositions without molecular sieves and microporous materials (example 1). In addition it demonstrates the need for appropriate selection of microporous materials with carrier

CLAIMS

1. A hair conditioner composition which is essentially anhydrous that comprises:

(a) one or more microporous materials each of which has an average pore size larger than the critical diameter of a water molecule;

(b) carrier molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials; and

(c) conditioner molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials.

2. A composition according to claim 1 wherein the microporous ingredient is an inorganic salts such as crystalline metal silicates selected from the group consisting of sodium aluminum potassium silicate, aluminum silicate, calcium aluminum silicate, activated alumina (aluminum oxide), diatomaceous silicas, bentonites, aluminum oxides, silicon oxides, and crystalline metal aluminosilicates.

3. A composition according to claim 2 wherein the microporous material is an aluminosilicate which ranges in average pore size from about 3 Angstroms to about 10 Angstroms.

4. A composition according to claim 1 wherein the microporous material is an activated charcoal.

5. A composition according to claim 1 wherein the carrier material is selected from the group consisting of hydrophilic glycols, polyethylene glycols, glycerin, and a polar solvent.

6. A composition according to claim 5 wherein the hydrophilic glycol is selected from the group consisting of propylene glycol, ethylene glycol, hexylene glycol, glycerin, sorbitol, butanediol, butylene glycol, and mixtures thereof.

7. A composition according to claim 5 wherein the polyethylene glycol is selected from the group consisting of PEGs -4, -6, -8, -9, -10, -12, -14, -16, -18, -20, -200, -400 and -600; beheneth -5 and -1 0; PEG-7 betanaphthol and PEG-1 5 butanediol; buteth-3 carboxylic acid, butoxynol-5 and -19, PEG-8 C12-18 ester, C12 -13 pareth-7 carboxylic acid, Cl 1 -15 pareth-7 carboxylic acid, C12 -15 pareth-7 carboxylic acid, C14 -15 pareth-8 carboxylic acid, PEG-8 caprate, PEG-8 caprylate, PEG-8 caprate/caprylate, PEG -6, and -8 caprylic/capric glycerides, capryleth -6 and -9 carboxylic acids, PEG-8 caprylatep; ceteareth -2, -3, -4, -5, -5, -6, -7, -8, -10, -11, -12, -13, -15, -6, -17, -18, and -20; choleth -1 0 and -20; PEG-3 cocamide, PEG-5 cocamide, PEG-6 cocamide, PEG-7 cocamide, PEG-1 1 cocamide, PEG-20 cocamide; PEG-2 cocamine, PEG-3 cocamine, PEG-5 cocamine, PEG-1 0 cocamine, PEG-1 5 cocamine, and PEG-20 cocamine; PEG-5 cocoate, PEG-8 cocoate, PEG-15 cocoate; coceth-3, 5, and -8; PEG-2 dilaurate, PEG-4 dilaurate, PEG-6 dilaurate, PEG-8 dilaurate, PEG-12 dilaurate, PEG-20 dilaurate, PEG-4 dioleate, PEG-6 dioleate, PEG-8 dioleate,

PEG-1 0 dioleate, PEG-12 dioleate, isostearеth-2, isostearеth-3, isostearеth-10, isostearеth-12, isostearеth-20; isoceteth- 10, and -20; isodeceth -4, -5, and -6; isostereath -2, -3, 1 0, 12, and -20; PEG-3 lauramine oxide; PEG-2 laurate, PEG-4 laurate, PEG-6 laurate, PEG-8 laurate, PEG-9 laurate, PEG-10 laurate, PEG-12 laurate, PEG-14 laurate, and PEG-20 laurate; laureth -1, -2, -3, -4, -5, -6, -7, -8, -9, -10, -11, -12, -13, -14, -15, 16,and -20; oleth 1, -3, -4, -5, -6, -7, -8, -9, -10, 12, -15, -16, and -20; stereath -2, -3, -4, -5, -6, -7, -10, -11, -13, -14, -15, -16, and -20; and trideceth -3, -5, -6, -9, -10, -11, -12, and -15.

8. A composition according to claim 5 wherein the polar solvent is selected from the group consisting of methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, isopropanol and mixtures thereof.

9. A composition according to claim 1 wherein the conditioner materials are selected from the group consisting of quaternary ammonium compounds, amidoamines, hydrophilic silicones, cationic polymers, hydrocarbons, fatty alcohols, and mixtures thereof.

10. A composition according to claim 9 wherein the silicone is selected from the group consisting of a polyalkyl siloxane, a polyaryl siloxane, a polyalkylaryl siloxane and mixtures thereof.

11. A composition according to claim 10 wherein the silicone is selected from the group consisting of a volatile

siloxane such as cyclotetrasiloxane, cylopentasiloxane, cyclohexasiloxane, or mixtures thereof.

12. A composition according to claim 1 0 wherein the silicone is a group of nonvolatile silicones consisting of dimethicone, dimethiconol, amodimethicone, phenyltrimethicone, silicone copolyol, and mixtures thereof.

13. A composition according to claim 9 wherein the cationic polymer is selected from the group consisting of: Guar hydroxypropyltrimonium chloride, poly(dimethyidiallylammonium chloride), poly(dimethyl butenyl ammonium chloride)- bis (triethanolammonium chloride), Poly (dipropyldiallylammonium chloride), Poly (methylbeta propaniodiallylammonium chloride), Poly (diallylpiperidinium chloride), Poly (vinylpyridinium chloride), quaternised poly (vinyl alcohol), quaternised poly(dimethylaminoethylmethacrylate) and mixtures thereof.

14. A composition according to claim 9 wherein the hydrocarbon is selected from the group consisting of nonane, octane, heptane, tert-pentane, dodecane, decahexane, decane, heptadecane, trimethylheptane, trimethylhexane, 4methylheptane, 4-methyldecane,isobutane, isopentane, isooctane, hexane, isododecane, isohexadecane, and mixtures thereof.

15. A composition according to claim 9 wherein the quaternary ammonium compound is selected from the group consisting of lauratrimonium chloride, quaternium -1 6, lauralkonium chloride, dicetyldimonium chloride, distearyl

dimonium chloride, behenyl dimonium chloride, cetylpyridinium chloride, soyatrimonium chloride, myristyltrimonium chloride, cetrimonium chloride, PEG-2 cocomonium chloride, PEG 2 cocoyl quaternium -4, PEG-2 oleyl quaternium-4, polyquaternium -6,-7, -11, -5, -24, and mixtures thereof.

16. A composition according to claim 14 wherein the amidoamine is selected from the group consisting of diethylaminoethylstearamide, isosteamidopropyldimethylamine, cocamidopropyldimethylamine, ricinoleamido propyldimethylamine, oleamidopropyldimethylamine, behenamidopropyldimethylamine, palmitamidopropyidimethylamine, stearamidylethyldiethylamine, soyamido propyidimethylamine and dimethylaminopropyl myristamide, stearamidylpropyl dimethylamine.

17. A composition according to claim 9 wherein the fatty alcohol is selected from the group consisting of stearyl alcohol, cetyl alcohol, behenyl alcohol, myristle alcohol, coco alcohol, and mixtures thereof.

18. A composition according to claim 1 which comprises:

| INGREDIENT | WEIGHT % |
|---|---|
| PEG 200 | 50.45 |
| CETEARYL ALCOHOL | 2.5 |
| BEHENTRIMONIUM CHLORIDE | 2.0 |
| STEARETH-2 | 1.0 |
| STEARETH-21 | 1.0 |
| PANTHENOL | 0.1 |
| GLYCERIN | 18.6 |
| CITRIC ACID | 0.7 |
| DIMETHICONE | 3.0 |
| SODIUM POTASSIUM ALUMINO-SILICATE 3 Angstroms | 20.0 |
| FRAGRANCE | 0.65 |

19. A method for conditioning hair with self warming which comprises applying to said hair an effective amount of a composition according to claim 1 and then applying to the hair water.

20. A method for conditioning hair with self warming which comprises applying to said hair water, and then applying to the hair an effective amount of a composition according to claim 1.

21. A hair shampoo composition which is essentially anhydrous that comprises:

(a) one or more microporous materials each of which has an average pore size larger than the critical diameter of a water molecule;

(b) carrier molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials; and

(c) shampoo molecules or molecular aggregates that have critical diameters larger than the average largest pore size of the microporous materials.

22. A method for shampooing hair with self warming which comprises applying to said hair water, and then applying to the hair an effective amount of a shampoo composition according to claim 21.

23. A method for shampooing hair with self warming which comprises applying to said hair an effective amount of a shampoo composition according to claim 21, and then applying to the hair water.

24. A hair shampoo and conditioner composition which is essentially anhydrous that comprises:

(a) one or more microporous materials each of which has an average pore size larger than the critical diameter of a water molecule;

(b) carrier molecules or molecular aggregates that have critical diameters larger than the average largest pore size of the microporous materials; and

(c) conditioner molecules or molecular aggregates that have critical diameters larger than the largest average pore size of the microporous materials;

(d) shampoo molecules or molecular aggregates that have critical diameters larger than the average largest pore size of the microporous materials.

25. A method for shampooing and conditioning hair with self warming which comprises applying to said hair water, and then applying to the hair an effective amount of a shampoo and conditioner composition according to claim 24.

26. A method for shampooing and conditioning hair with self warming which comprises applying to said hair an effective amount of a shampoo and conditioner composition according to claim 24, and then applying to the hair water-

27. A composition in accordance with claim 1, wherein the average pore size is from about 3 Angstroms to about 13 Angstroms.

28. A composition in accordance with claim 1, wherein th average pore size is from about 3 Angstroms to about 10 Angstroms.

# INTERNATIONAL SEARCH REPORT

Ir. ational Application No
PCT/EP 99/10168

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/00 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| P,X | EP 0 897 719 A (UNILEVER PLC ;UNILEVER NV (NL)) 24 February 1999 (1999-02-24) page 6, line 45,46 claims 1,6; example 1 --- | 1-3,5-7, 19,27,28 |
| X | US 3 702 302 A (WILSON VERNON COLUMBUS) 7 November 1972 (1972-11-07) column 3, line 1-30 column 4, line 1-30 column 4, line 47-54 --- | 1-3,5,7, 27,28 |
| X | EP 0 586 929 A (KAO CORP) 16 March 1994 (1994-03-16) claims 1,17; example 4 --- -/-- | 1-3,5-7, 9,10,12, 15,19, 27,28 |

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 17 April 2000 | 11/05/2000 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 | Sierra Gonzalez, M |

Form PCT/ISA/210 (second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/10168

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | H.F. MARK: "KIRK - OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY. vol 15" 1978 XP002133448 page 638 -page 660; table 6 --- | 1-20,27, 28 |
| A | H.F. MARK: "Kirk-Othmer Encyclopedia of Chemical Technology" XP002133449 page 115 page 122-124 --- | 1-20,27, 28 |
| A | H.F. MARK: KIRK-OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY , vol. 1, 1978, pages 563-564, XP002133655 ----- | 1-20,27, 28 |

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 99/10168

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: -
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
See FURTHER INFORMATION SHEET PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-17, 19-20 and 27-28 (partially); 21-26 (not searched)

Present claims 1-17 and 19-20 and 27-28 relate to a composition defined by reference to the following parameters of the constituent compounds:

P1: critical diameter of the water molecule
P2: average pore size of microporous materials
P3: critical diameter of the carrier molecules
P4: critical diameter of the conditioner molecules

and by the following ratios:

P2/P1
P3/P2
P4/P2

The use of these parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible.

Furthermore, the term "molecular aggregates" is obscure. It has not been disclosed in the application in a manner sufficiently clear and complete to allow the skilled man to understand the application (Article 5 PCT). It is doubtful whether the critical diameter refers to the molecule or to the molecular aggregate.

Moreover, the term "shampoo molecules" of claims 21-26 it is not usual in the art and it is not clear to the skilled person. It also has not been disclosed in the application in a manner sufficiently clear and complete to allow the skilled person to understand the application (Article 5 PCT). As a consequence and considering also the above mentioned objections to clarity (to the parameters and to the term "molecular aggregate") a meaningful search of these particular claims is considered to be impossible. Claims 21-26 have not been searched.

Consequently, the search has been restricted to a composition comprising one or more microporous materials (as defined in the description, page 5, line 10-page 6, line 7), carrier molecules (as defined on page 6, line 26-page 8, line 16) and conditioner molecules (as defined on page 8, line 22-page 13, line 11), as defined completely in the claims with due regard to the general idea underlying the application.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Ir. ational Application No
PCT/EP 99/10168

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP 0897719 A | 24-02-1999 | CA 2244591 A | 19-02-1999 |
| | | JP 11116463 A | 27-04-1999 |
| US 3702302 A | 07-11-1972 | NONE | |
| EP 0586929 A | 16-03-1994 | DE 4227203 A | 07-10-1993 |
| | | DE 9211006 U | 16-12-1993 |
| | | AT 110955 T | 15-09-1994 |
| | | DE 69300008 D | 13-10-1994 |
| | | DE 69300008 T | 26-01-1995 |
| | | JP 7069835 A | 14-03-1995 |
| | | US 5538720 A | 23-07-1996 |